Safety Data Sheet

Chromium and compounds

Division of Safety
National Institutes
of Health

WARNING!

SOME COMPOUNDS IN THIS CLASS ARE TOXIC, CARCINOGENIC, AND MUTAGENIC. THEY ARE READILY ABSORBED BY VARIOUS BODY TISSUES THROUGH THE RESPIRATORY AND INTESTINAL TRACTS. THEY MAY CAUSE SEVERE IRRITATION OF TISSUES (SKIN, EYES, MUCOUS MEMBRANES, AND LUNGS) AND INDUCE SENSITIVITY. AVOID FORMATION AND BREATHING OF AEROSOLS OR MISTS.

LABORATORY OPERATIONS SHOULD BE CONDUCTED IN A FUME HOOD, GLOVE BOX, OR VENTILATED CABINET.

AVOID SKIN CONTACT: IF EXPOSED, WASH WITH DILUTE SODIUM BISULFITE SOLUTION FOLLOWED BY WATER. AVOID RUBBING OF SKIN OR INCREASING ITS TEMPERATURE.

FOR EYE EXPOSURE, IRRIGATE IMMEDIATELY WITH LARGE AMOUNTS OF WATER. FOR INGESTION, INDUCE VOMITING. DRINK MILK, 1% SODIUM THIOSULFATE SOLUTION, OR WATER. REFER FOR GASTRIC LAVAGE. FOR INHALATION, REMOVE VICTIM PROMPTLY TO CLEAN AIR. ADMINISTER RESCUE BREATHING IF NECESSARY. REFER TO PHYSICIAN.

IN CASE OF LABORATORY SPILLS, WEAR PROTECTIVE CLOTHING DURING CLEANUP. AVOID SKIN CONTACT AND BREATHING OF AEROSOLS. USE WATER OR DILUTE MINERAL ACID TO DISSOLVE COMPOUND. USE ABSORBENT PAPER TO MOP UP SPILL. WASH DOWN AREA WITH WATER (SOLUBLE CHROMIUM SALTS) OR DILUTE MINERAL ACID FOLLOWED BY WATER (ALL OTHERS). DISPOSE OF WASTE SOLUTIONS AND MATERIALS APPROPRIATELY. MONITOR LABORATORY AIR AND CHECK FOR CHROMIUM RESIDUES AFTER CLEANUP.

A. Background

Metallic chromium is steel-gray and of considerable hardness. Cr(III) compounds are crystalline materials of various colors, chromates are yellow, and dichromates are orange to red. Cr(VI)

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compounds are toxic in animals and humans, producing irritation of the skin and respiratory tract and ulceration or perforation of the nasal septum; some are carcinogenic and mutagenic. Cr(III) compounds are far less toxic and noncorrosive. In epidemiological studies, inhalation of dusts or fumes of chromium compounds has been associated with increased incidence of lung cancer.

Chromium and its compounds exist in a variety of valence states: from -2 to +7. The biologically significant ones are 0 (chromium metal), +3 (chromic compounds), possibly +5, and +6 (chromates, dichromates). Chromous compounds (valence +2) are strong reducing agents and are not found in nature; chromium dioxide (valence +4) is used in magnetic recording tapes but there is no information on its biological effects. As groups, chromium compounds with valence +3 and +6 will be referred to as Cr(III) and Cr(VI) compounds, respectively.

Chromium compounds in low concentrations are an essential element in the animal diet; chromium deficiency results in impairment of glucose metabolism. Commercially, the chief uses of chromium and its compounds are in the production of stainless steels, as abrasives, in the tanning of leather, as pigments, and in textile printing.

The current permissible exposure limits to chromium compounds in air have been tabulated by Sittig (1985) and are as follows: Chromic acid and chromates: 30 mg/m^3; chromium metal and insoluble salts: 500 mg/m^3; soluble chromic and chromous salts: 250 mg/m^3. Current 8 hour time-weighted averages are: chromium metal, Cr(II), and Cr(III) compounds: 0.5 mg/m^3; Cr(VI) compounds (both soluble and insoluble): 0.05 mg/m^3; chromyl chloride: 0.15 mg/m^3.

Recent reviews of the chemical and biological properties of chromium include: Léonard and Lauwerys, 1980; Langård, 1982; IARC, 1980, 1982; Hertel, 1986.

Chemical and Physical Properties

For properties not listed under individual entries, see the end of this section.

Chromium

1. Chemical Abstract No.: 7440-47-3

2. Chemical formula: Cr; atomic weight: 51.996.

3. Density: 7.20 g/cm^3 at 28°C.

4. Solubility: Insoluble in water, nitric acid, and aqua regia (made passive by these acids and by other oxidizing agents such as chlorine and bromine).

5. Description: Steel gray, lustrous metal.

6. Boiling point: 2,672°C.

   Melting point: 1,857 ± 20°C.

7. Stability: Stable at ambient temperatures.

8. Chemical reactivity: Reacts slowly with dilute hydrochloric and sulfuric acids. "Activated" by reducing agents such as hydrogen gas.

Barium chromate

1. Chemical Abstract No.: 10294-40-3

2. Synonyms:

Lemon chrome	Steinbuehl yellow
Lemon yellow	C.I. pigment yellow 31
C.I. 77103	Ultramarine yellow
Baryta yellow	Chromic acid [H_2CrO_4], barium salt (1:1) (9CI)

3. Chemical formula: $BaCrO_4$; molecular weight: 253.33

4. Solubility: Practically insoluble in water (4.4 mg/l at 28°C).

5. Description: Yellow crystals.

6. Chemical reactivity: Reacts with dilute mineral acids.

Calcium chromate (dihydrate)

The usual form of calcium chromate is the dihydrate, and data given here are for this compound. The anhydrous, hemihydrate, and monohydrate forms are also known. It is not always clear whether the "synonyms" listed below refer to the anhydrous salt or the dihydrate.

1. Chemical Abstract No.: 10060-08-9

2. Synonyms:

Gelbin	Yellow ultramarine	Calcium chromate (VI)
C.I. 77223	Calcium chromate yellow	C.I. pigment yellow 33

Chromic Acid, calcium salt, (1:1), dihydrate (9CI)

3. Chemical formula: $CaCrO_4.2H_2O$; molecular weight: 192.1

4. Solubility: Soluble in water (16.3 g/100 ml at 20°C) and ethanol.

5. Description: Yellow crystals.

6. Stability: Loses water of hydration at 200°C.

7. Chemical reactivity: Reacts with dilute mineral acids.

"Sintered calcium chromate"

This is the product of heating calcium chromate at 2,000°F for one hour. In the process, a variable part of the chromate is reduced t lower valences, and the result is an undefined mixture of compounds (Hueper and Payne, 1959).

Chromic chloride

1. Chemical Abstract No.: 10025-73-7

2. Synonyms:

Chromium(III) chloride

C.I. 77295 Chromium chloride ($CrCl_3$) (9CI)

3. Chemical formula: $CrCl_3$; molecular weight: 158.35

4. Solubility: The anhydrous form is practically insoluble in col water except in the presence of wetting agents; the hexahydrate is very soluble (58.5 g/100 ml). Various isomers of hexahydrat are known and their solubilities are listed by Windholz (1983).

5. Description: Violet crystalline scales.

6. Melting point: 1,150°C; sublimes at 1,300°C.

7. Stability: Deliquesces in moist air.

Chromic oxide

1. Chemical Abstract No.: 1308-38-9

2. Synonyms:[A]

C.I. 77288	Green cinnabar	C.I. pigment green 17
Anadonis green	Chromium(III) oxide	Chromium oxide (Cr_2O_3)(9CI)
Chromium sesquioxide		

[A] For other commercial synonyms see IARC (1980).

3. Chemical formula: Cr_2O_3; molecular weight: 152.02

4. Solubility: Practically insoluble in water.

5. Description: Light to dark green fine crystals.

6. Boiling point: about 3,000°C (Windholz, 1983).

   Melting point: about 2,435°C (Windholz, 1983).

7. Stability: No data; assumed to be stable under ambient conditions.

8. Chemical reactivity: Reacts slowly with dilute acids and alkalis.

Chromium trioxide

1. Chemical Abstract No.: 1333-82-0

2. Synonyms:

   Chromium(VI) oxide Chromic(VI) acid anhydride

   Chromium oxide (CrO_3) (9CI)

3. Chemical formula: CrO_3; molecular weight: 99.99

4. Solubility: Very soluble in water (61.7 g/100 ml at 0°C); soluble in sulfuric and nitric acids.

5. Description: Dark red deliquescent crystals or powder.

6. Melting point: 196-197°C.

7. Stability: Decomposes at 250°C to $Cr_2O_3 + O_2$. Unstable in the presence of most organic compounds.

8. Chemical reactivity: Powerful oxidizing agent. Contact with combustible material may cause fire or explosion.

Lead chromate

1. Chemical Abstract No.: 7758-97-6

2. Synonyms:[A]

   Crocoite C.I. 77600

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other commercial synonyms see IARC (1980).

Paris yellow — King's yellow

Chrome yellow — Chromic acid (H_2CrO_4), lead(2+) salt (1:1) (9CI)

3. Chemical formula: $PbCrO_4$; molecular weight: 323.18

4. Solubility: Practically insoluble in water (0.058 mg/100 ml at 25°C (considered to be one of the most insoluble salts).

5. Description: Yellow or orange-yellow crystalline powder.

6. Melting point: 844°C.

7. Stability: Decomposes on heating above melting point.

8. Chemical reactivity: Reacts with mineral acids and alkalis.

Sodium chromate

1. Chemical Abstract No.: 7775-11-3

2. Synonyms:

   Chromic acid (H_2CrO_4), disodium salt (9CI)

3. Chemical formula: Na_2CrO_4; molecular weight: 161.97[A]

4. Solubility: Highly soluble in water (87.3 g/100 ml at 30°C) soluble in methanol; slightly soluble in ethanol.

5. Description: Yellow crystals.

6. Melting point: 792°C.

7. Stability: Stable in the absence of moisture.

8. Chemical reactivity: Sodium chromate solutions in water are alkaline; on addition of acid they change to dichromate:
   $$2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$
   The position of the equilibrium depends on pH; this also accounts for the change in color from yellow (chromate) to orange-red (dichromate) on acidification and for the high oxidizing power of sodium chromate in acid solution. In the presence of organic matter, sodium chromate (and dichromate) readily reduced to Cr(III) compounds.

Sodium dichromate (dihydrate)

1. Chemical Abstract No.: 7789-12-0

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lso exists as stable tetrahydrate and deliquescent decahydrate.

2. Synonyms:

   Sodium bichromate

   Chromic acid ($H_2Cr_2O_7$), disodium salt, dihydrate, (9CI)

3. Chemical formula: $Na_2Cr_2O_7.2H_2O$; molecular weight: 298.00

4. Solubility: Highly soluble in water (70.6 g/100 ml at 0°C) and methanol.

5. Description: Reddish to bright orange, somewhat deliquescent crystals.

6. Melting point: Becomes anhydrous on prolonged heating at about 100°C; the anhydrous salt melts at 356.7°C and decomposes at 400°C.

7. Stability: Stable at ambient temperature.

8. Chemical reactivity: See under "sodium chromate." Aqueous solutions are acidic (1% solution has a pH of 4).

Other properties. There are no data for any of the above compounds regarding optical absorption characteristics, volatility, flash point, autoignition temperature, or explosive limits.

Other compounds. The chromium compounds listed above are, for the most part, single representatives of each class of compounds of biological interest. Chemical and physical properties of many others may be found in Weast (1983) and IARC (1980).

Fire, Explosion, and Reactivity Hazard Data

1. Fire fighters should wear protective clothing and a full-facepiece, self-contained breathing apparatus in positive-pressure mode. Contact with some chromium compounds is irritating to the skin and mucous membranes. While chromium compounds are not flammable themselves (with the exception of ammonium dichromate), fire can produce toxic products. In the case of chromium trioxide, contact with combustible materials may result in fire or explosive hazards.

2. Conditions contributing to instability of Cr(VI) compounds include heat and the presence of reducing materials (paper, wood, sulfur, aluminum, plastics, etc.)

3. No other incompatibilities have been reported.

4. Chromium compounds (with the possible exception of chromium trioxide, for which no pertinent data exist) do not require nonspark equipment.

Operational Procedures

The NIH Guidelines for the Laboratory Use of Chemical Carcinogens describe operational practices to be followed when potentially carcinogenic chemicals are used in NIH laboratories. The NIH Guidelines should be consulted to identify the proper use conditions required and specific controls to be implemented during normal and complex operations or manipulations involving chromium compounds.

It should be emphasized that this data sheet and the NIH Guidelines are intended as starting points for the implementation of good laboratory practices when using these compounds. The practices and procedures described in the following sections pertain to the National Institutes of Health and may not be universally applicable to other institutions. Administrators and/or researchers at other institutions should modify the following items as needed to reflect their individual management system and current occupational and environmental regulations.

1. Chemical inactivation: No validated method reported.

2. Decontamination: Turn off equipment that could be affected by chromium compounds or the materials used for cleanup. If there is any uncertainty regarding the procedures to be followed for decontamination, call the NIH Fire Department (dial 116) for assistance. Use absorbent paper to mop up spill. Wipe off surfaces with acidified water, then wash with copious quantities of water. Glassware should be rinsed (in a hood) with acidified water, followed by soap and water. Animal cages should be washed with water.

3. Disposal: No waste streams containing chromium compounds shall be disposed of in sinks or general refuse. Surplus chromium compounds or chemical waste streams contaminated with chromium compounds shall be handled as hazardous chemical waste and disposed of in accordance with the NIH chemical waste disposal system. Nonchemical waste (e.g., animal carcasses and bedding) containing chromium compounds shall be handled and packaged for incineration in accordance with the NIH medical-pathological waste disposal system. Potentially infectious waste (e.g., tissue cultures) containing chromium compounds shall be disinfected by heat using a standard autoclave treatment and packaged for incineration, as above. Burnable waste (e.g., absorbent bench top liners) minimally contaminated with chromium compounds shall be handled as potentially infectious waste and packaged for incineration, as above. Absorbent materials (e.g., associated with spill cleanup) grossly contaminated shall be handled in accordance with the chemical waste disposal system. Radioactive waste containing chromium compounds shall be handled in accordance with the NIH radioactive waste disposal system.

4. Storage: Store solid chromium compounds and their solutions in dark-colored, tightly closed containers. Avoid contact with reducing materials and/or atmospheric moisture for those chromium compounds where this is indicated (see entries under "stability" in B above for individual compounds).

Monitoring and Measurement Procedures Including Direct Field Measurements and Sampling for Subsequent Laboratory Analysis

Methods for sampling, sample preparation and analysis have been critically reviewed (Beyermann, 1962; NAS, 1974; NIOSH, 1975; Hubert, 1979; IARC, 1986).

1. Sampling: The officially recommended method for air sampling of Cr(VI) compounds is filtration through polyvinyl chloride filters (Abell and Carlberg, 1974; NIOSH, 1987); the use of this filter material rather than filter paper avoids possible partial reduction on the filter to Cr(III). No specific method for air sampling of Cr(III) compounds has been described, but the NIOSH method is probably applicable. Hubert (1979) discusses sources of possible high (contamination from containers, reagents, or needles) or low (loss on wet or dry ashing) results of chromium determination due to faulty sampling.

2. Analysis: Most analytical procedures have been developed for the measurement of Cr(VI) or for total chromium after oxidation. The officially recommended colorimetric method is based on the formation of a stable colored complex of Cr(VI) with sym-diphenylcarbazide (Abell and Carlberg, 1974; NIOSH, 1987). The lower detection limit is 3.5 ng Cr. While this method is usually not sensitive enough for determination of chromium in normal biological materials, its sensitivity has been extended by means of long-path microcuvettes (Yarbro and Flaschka, 1976). Gas chromatography is somewhat more sensitive than other methods but more subject to interfering substances; an application to the determination of Cr(III) in urine has been described (Ryan and Vogt, 1977). Preferred methods are based on flameless atomic absorption and have been applied to blood, tissues and urine (Tessari and Torsi, 1972; Davidson and Secrest, 1972) either directly or (preferably) after wet ashing with perchloric acid followed by hydrogen peroxide or with a mixture of nitric, perchloric, and sulfuric acid (Chao and Pickett, 1980).

   The determination of both Cr(III) and Cr(VI), based on differences of extractability with pH, has been described for sea water (DeJong and Brinkman, 1978) but should also be adaptable to biological materials. A sophisticated four-stage differential procedure for analysis of chromium in air-borne dust determines total Cr, water-soluble Cr(VI), and the size, shape, and surface oxidation state of the dust particles (Bohgard et al., 1979). Typical methods for analysis of environmental samples have been tabulated (IARC, 1980, 1986).

Other methods, not used as widely, include neutron activation analysis and X-ray fluorescence.

Biological Effects (Animal and Human)

Biological and toxicological effects of chromium have been reviewed (Mertz, 1969; NAS, 1974; various chapters in Langård, 1982).

1. Absorption: The rate and degree of absorption of chromium compounds from the gastrointestinal tract depend on the valence state and the pH of the environment. The presence or absence of food in the stomach is also important since food constituents reduce Cr(VI) to Cr(III), which is very poorly absorbed and does not cross biological membranes, while water-soluble Cr(VI) compounds do. Cr(VI) compounds do not penetrate skin as such but are reduced to Cr(III) compounds, which form complexes with skin proteins (Burrows, 1979). Inhaled chromium dust is tightly bound to lung tissue and produces local effects. Significant systemic absorption by this route is questionable except for water-soluble chromates, which quickly disappear from lung tissue after inhalation.

2. Distribution and pharmacokinetics: Water-soluble Cr(VI) compounds (chromates), after penetration to the bloodstream, are carried in the red blood cells probably after reduction, while Cr(III) compounds are bound to serum proteins, particularly to siderophilin (transferrin), a β-globulin, from which they are transported to the tissues. Injection of tracer doses of Cr(III) chloride results in high concentrations in ovaries, spleen, kidney, and liver. In contrast to other trace metals, chromium in these tissues is associated primarily with cell nuclei. Injected Cr(III) and Cr(VI) in liver and kidney of rats are bound mainly to DNA, the non-histone protein of chromatin, and cytoplasmic RNA, though entry into these organs is much slower after administration of Cr(III) than of Cr(VI) (Tsapakos et al., 1983; Cupo and Wetterhahn, 1985). In man, injection of labeled Cr(III) chloride results in major concentration in liver, spleen, soft tissue, and bone; a pharmacokinetic model of a plasma pool in equilibrium with three compartments has been developed (Lim et al., 1983).

3. Metabolism and excretion: Small concentrations of chromium are a nutritional requirement, and its exclusion from the diet of animals has a profound effect on carbohydrate metabolism (impairment of glucose tolerance and production of diabetes-like symptoms); the mechanism of this action appears to be a potentiation of insulin action which has been demonstrated both *in vivo* and *in vitro*, resulting in increased blood insulin levels, increased mobilization from storage sites, and therefore insulin depletion (Shapcott and Hubert, 1979; Li and Vallee, 1980). *In vitro* experiments show that the binding of Cr(VI) to DNA requires the presence of a reducing system while binding of

Cr(III) does not; since Cr(III) has little or no toxicity, it has been suggested that an intermediary oxidation state is responsible for maximal binding to DNA (Tsapakos and Wetterhahn, 1983) and indeed there is evidence for the formation of Cr(V) from Cr(VI) in the presence of the same reducing system (Jennette, 1982).

Excretion of injected chromium is mainly in the urine, while that of ingested chromium (particularly Cr(III) and water-insoluble chromates) is in feces. Corroborating evidence has been shown in two human subjects (Offenbacher et al., 1986).

Toxic effects: There are very few data on the LD50 of chromium compounds. In general, Cr(III) compounds have very low toxicity (LD50, oral, rat, of chromic nitrate nonahydrate = 1.54 g/kg; median lethal dose, intravenous, mouse, of chromic chloride = 400-800 mg/kg); no toxic effects were noted when rats received 25 ppm of Cr(III) in drinking water over a period of one year. Similar doses of Cr(VI) are also tolerated, but at higher concentrations toxic effects are noted. Ingested Cr(VI) is irritating and corrosive to mucous membranes of the gastrointestinal tract, resulting in vomiting, diarrhea, gastric and intestinal hemorrhage, and kidney damage. The latter is the most common lesion after subcutaneous and intravenous injection and appears chiefly in the form of tubular nephritis. Occupational exposure in humans to chromium dusts results in coughing and wheezing, headaches, and bronchial irritation, which persists after other symptoms subside. Sensitization to subsequent exposures may develop. Prolonged inhalation leads to irritation and ulceration of the nasal septum. Particularly noteworthy are the effects of accidental contamination by chromates and dichromates on the skin, which include corrosive actions (ulcers, scars) and sensitization (allergic contact dermatitis). While it is more difficult to produce these reactions with Cr(III) (20-50 times higher dose is required) it nevertheless appears that Cr(VI) is reduced in the skin to Cr(III) and that this is the causative species, owing to its ability to form complexes with skin proteins (NAS, 1974; Burrows, 1979).

Carcinogenic effects: A vast amount of literature concerning the carcinogenicity of chromium compounds in animals has recently been tabulated and discussed (IARC, 1980; Hayes, 1982). Some of these data are contradictory, especially where experiments were performed with materials of ill-defined composition, such as "sintered calcium chromate" (see Section B), "mixed chromate dust," and "roasted chromate ore." The following general conclusions may be drawn tentatively:

a. Highly water-soluble Cr(VI) compounds (such as alkali chromates and dichromates, chromium trioxide) are noncarcinogenic.

b. Water-soluble Cr(III) compounds (such as chromic chloride and sulfate) are noncarcinogenic.

c. Cr(VI) compounds of moderate or low water solubility produce malignant and nonmalignant tumors, almost exclusively at the site of injection or implantation (intrapleural, intramuscular). Outstanding examples are calcium chromate and lead chromate. The latter provides the only case in which carcinomas (renal) other than at t injection site (intramuscular) have been reported. Chromates of zinc and strontium also fall into this category.

d. The carcinogenicity of chromium powder and chromic oxide questionable. Epidemiological studies of workers exposed in chromate-producing, chromate pigment, and chromium plating industries (e.g., Baetjer, 1950a, 1950b; Bidstrup and Case, 1956; Langård and Norseth, 1975) are discussed detail in IARC (1980). A high incidence of lung cancer ha been noted repeatedly among workers in the first two industries. In more recent years the incidence has decreased because of more stringent environmental control measures but has not been eliminated, particularly on prolonged exposure.

Inhaled or intratracheally instilled sodium dichromate and pyrolyzed chromium oxide produced no carcinogenic effects in long-term experiments (Glaser et al., 1986; Steinhoffer et al., 1986).

On the basis of available evidence, an IARC Working Group has reached the following conclusions:

> "Evidence for carcinogenicity to humans - sufficient; Evidence for carcinogenicity to animals - sufficient; Evidence for activity in short term tests - sufficient for Cr(VI), inadequate for Cr(III)." (IARC, 1982)

6. Mutagenic and teratogenic effects: These have been reviewed in detail (Levis and Bianchi, 1982; Bianchi et al., 1983). The general conclusion is that Cr(III) compounds are not mutagenic in the Ames test or against E. coli, while all Cr(VI) compounds tested (chromates or dichromates of varying solubility) are highly mutagenic. Teratogenicity has not been reported.

Emergency Treatment

1. Skin and eye exposure: For skin exposure, remove contaminated clothing and wash skin with dilute sodium bisulfite solution followed by water. Avoid rubbing of skin or increasing its temperature. For eye exposure, irrigate immediately with copious quantities of running water for at least 15 minutes. Obtain ophthalmological evaluation.

2. Ingestion: Drink 1% sodium thiosulfate solution, water, or milk. Induce vomiting. Refer for gastric lavage.

3. Inhalation: Remove victim promptly to clean air. Administer rescue breathing if necessary.

4. Refer to physician at once. Consider treatment for pulmonary irritation.

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